

A SYSTEM AND A METHOD OF SOLID STORAGE AND DISSOLUTION OF
A CATHOLYTE FOR USE IN ELECTROCHEMICAL CELL

TO ALL WHOM IT MAY CONCERN:

BE IT KNOWN THAT (1) STEVEN P. TUCKER, (2) MARIA G. MEDEIROS, and (3) ERIC G. DOW, employees of the United States Government, citizens of the United States of America, and residents of (1) Portsmouth, County of Newport, State of Rhode Island, (2) Bristol, County of Bristol, State of Rhode Island and (3) Barrington, Bristol County, Rhode Island have invented certain new and useful improvements entitled as set forth above of which the following is a specification:

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3 A SYSTEM AND A METHOD OF SOLID STORAGE AND DISSOLUTION OF
4 A CATHOLYTE FOR USE IN ELECTROCHEMICAL CELL
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6 STATEMENT OF GOVERNMENT INTEREST

7 The invention described herein may be manufactured and used
8 by or for the Government of the United States of America for
9 Governmental purposes without the payment of any royalty thereon
10 or therefor.
11

12 BACKGROUND OF THE INVENTION

13 (1) Field Of The Invention

14 This invention relates to semi fuel electrochemical cells
15 used for undersea vehicle propulsion. Specifically, this
16 invention relates to a system and a method for solid storage and
17 subsequent dissolution of electrolytes/catholytes used in semi
18 fuel electrochemical cells used for undersea vehicle propulsion.

19 More specifically, this invention relates to a system and a
20 method for solid storage and subsequent dissolution of
21 electrolytes/catholytes, wherein a solid medium is provided
22 comprising electrolytes/catholytes in a solid form and includes
23 sodium peroxide particles suspended in a matrix of potassium
24 superoxide and/or sodium hydroxide, wherein the matrix controls
25 the dissolution and hydrolysis rate of the solid catholyte by

1 allowing for a dissolution only from a controlled surface of the
2 solid medium, and wherein the matrix itself is dissolved and
3 hydrolyzed and the products of this dissolution and hydrolysis
4 are usable by the semi fuel cell.

5 (2) Description Of The Prior Art

6 Primary batteries employing caustic electrolytes with
7 hydrogen peroxide as the cathode species have been under
8 development by the Navy and other laboratories since the 1980s.
9 The aluminum-hydrogen peroxide semi fuel cells have applications
10 in torpedoes, unmanned undersea vehicles ("UUVS") and other
11 undersea craft that utilize electric energy. Emphasis has been
12 placed on cost reduction in utilizing hydrogen peroxide as the
13 cathode as opposed to earlier silver oxide cathodes. In order to
14 achieve high energy storage densities it has been necessary to
15 consider storing all reactants in concentrated form. Limiting
16 factors in the development of the semi fuel cell systems,
17 however, are the safety issues associated with liquid hydrogen
18 peroxide and the total mass of hydrogen peroxide that would be
19 required to be stored for a given mission.

20 Research has been conducted in an effort to avoid the
21 problems related to liquid hydrogen peroxide as a catholyte. For
22 example, use of oxygen as the cathode species employing an oxygen
23 reduction cathode membrane has been investigated, developed and
24 demonstrated for use undersea (with bottled oxygen or oxygen
25 candles) and on land (using air as the oxygen source). However,

1 there is a need for higher energy densities than those that have
2 been achieved by these methods. Additionally, as with
3 concentrated hydrogen peroxide, there are also safety concerns
4 associated with each of these systems.

5 Other forms of concentrated catholyte for fuel cell systems
6 that have been investigated for high energy storage densities are
7 catholytes delivered to catholyte solutions from solid form, for
8 example, powders or pellets. However, these forms for delivering
9 catholytes render control of the dissolution rate of the solid
10 catholyte composition into the aqueous electrolyte difficult.
11 Although catholyte rate delivery can be attained, to some degree,
12 by adjusting the geometrical size and shape of the catholyte
13 composition, the degree of control is too imprecise to properly
14 control the dissolution of the catholyte when its shape and size
15 varies during its lifetime. A related problem is posed by
16 dissolution rate sensitivity of solid catholytes to the flow rate
17 of the catholyte solution.

18 Attempts to solve the problems associated with solid
19 electrolytes and the control of their dissolution and hydrolysis
20 have been made. For example, U.S. Patent No. 5,399,444 to Smith
21 discloses a device that operates based on the stated discovery
22 that the concentration of an electrolyte in solution can be
23 maintained even when the electrolyte is being consumed
24 continuously or intermittently by utilizing an electrolyte
25 delivery system based upon internal osmotic pressure. The device

1 employs salts as solid electrolytes, for example sea salt and
2 zinc chloride, or bases such as lithium hydroxide, sodium
3 hydroxide, and potassium hydroxide or mixtures thereof.
4 Particles of electrolytes are coated with a semi-permeable
5 coating. Water is imbibed through the coating and dissolves the
6 water-soluble electrolyte, thereby creating an osmotic pressure
7 that causes the saturated solution of the electrolyte to be
8 pumped out the micro-passageways in the film coating. By
9 adjusting the relative amount of electrolyte solution to solid
10 electrolyte in the delivery, one can maintain the concentration
11 of the electrolyte in solution relatively constant during the use
12 of the electrolyte solution in an electrochemical apparatus.

13 U.S. Patent No. 5,529,707 to Kejha discloses solid composite
14 polymeric electrolytes that are made by mixing alkali metal
15 trifluoromethanesulfonate and polyethylene oxide to which
16 mixtures of lightweight non-conductive inorganic fillers such as
17 oxides or peroxides of lithium, magnesium, and sodium have been
18 added with co-solvents of esters and ethers. Solidification of
19 the electrolyte is achieved by the presence of the alkali metal
20 trifluoromethanesulfonate and by partial evaporation of the lower
21 boiling point ether or ester. These electrolytes can be used as
22 solid, semi-solid or liquid state polymer electrolytes for
23 batteries and other electrochemical devices.

24 None of the above prior art address the problems related to
25 catholytes where the cathode species is hydrogen peroxide

1 obtained by dissolution of caustic oxides, peroxides, or
2 superoxides and which are an alternative to liquid hydrogen
3 peroxide and provide the required high energy densities for semi
4 fuel cells in underwater vehicles. Thus, powdered or crystalline
5 forms of these peroxides, oxides, and superoxides dissolve
6 rapidly in water with an exothermic reaction. It is necessary to
7 control the hydrolysis rate of these solid catholytes to avoid
8 decomposition of hydrogen peroxide as the heat that is generated
9 during the hydrolysis destabilizes hydrogen peroxide before it
10 reaches the fuel cell.

11 Consequently there is a need in the art for an inexpensive
12 system and method that utilizes solid catholytes such as oxides,
13 peroxides and superoxides of alkaline metals in which the rate of
14 hydrolysis is controlled to limit the production of cathode
15 species (H_2O_2) to the rate at which they are consumed in the semi
16 fuel cell.

18 SUMMARY OF THE INVENTION

19 The object of this invention is to provide an inexpensive
20 system and method that does not pose high safety risks related to
21 the storage of liquid hydrogen peroxide by utilizing solid
22 catholytes such as oxides, peroxides, and superoxides of alkaline
23 metals and which provides for a controlled rate of catholyte
24 hydrolysis to limit the production of cathode species (H_2O_2) to
25 the rate at which they are consumed in a semi fuel cell.

1 In accordance with this invention there is provided a solid
2 medium for storing a solid catholyte wherein catholyte particles
3 are suspended within a matrix of encapsulating species.
4 Specifically, there is provided a solid medium for storing a
5 solid catholyte wherein catholyte particles are selected from
6 oxides, superoxides and peroxides of alkaline metals and the
7 encapsulating species are selected from oxides, superoxides, and
8 peroxides of alkaline metals and sodium hydroxide. Preferably,
9 the solid medium comprises sodium peroxide (Na_2O_2) as catholyte
10 particles encapsulated in a matrix of potassium superoxide and/or
11 sodium hydroxide (KO_2 and/or NaOH). The solid medium includes a
12 controlled surface where hydrolysis resulting in products that
13 include hydrogen peroxide, is to occur.

14 In accordance with this invention there is also provided a
15 high energy density system including a solid medium comprising
16 catholyte particles suspended within the encapsulating species,
17 wherein the rate of dissolution and hydrolysis of the solid
18 catholyte is controlled by the encapsulating species by allowing
19 for dissolution and hydrolysis to occur only on a controlled
20 surface of the medium, wherein the encapsulating species is
21 dissolved and hydrolyzed and used up for the operation of a fuel
22 cell, and wherein products of hydrolysis of catholyte particles
23 and encapsulating species include hydrogen peroxide.

24 In accordance with this invention there is also provided a
25 high energy density system including a solid medium comprising

1 sodium peroxide particles, as a solid catholyte particles,
2 suspended within the matrix of potassium superoxide and/or sodium
3 hydroxide, wherein the rate of dissolution and hydrolysis of the
4 solid catholyte is controlled by the encapsulating species of the
5 matrix in that the encapsulating species creates a controlled
6 surface of the solid medium and the dissolution and hydrolysis
7 occur only on the controlled surface of the medium, wherein the
8 encapsulating species is dissolved and hydrolyzed and used up for
9 the operation of a fuel cell, and wherein products of hydrolysis
10 of catholyte particles and encapsulating species include hydrogen
11 peroxide.

12 In accordance with this invention there is further provided
13 a method of making a catholyte solution comprising hydrogen
14 peroxide, including the steps of fabricating a solid medium
15 comprising catholyte particles suspended within a matrix of
16 encapsulating species, wherein the solid medium has a controlled
17 surface, dissolution of the solid catholyte and encapsulating
18 species in a liquid circulating across the controlled surface of
19 the medium, wherein said matrix controls the rate of the
20 dissolution and hydrolysis of the solid catholyte by allowing for
21 dissolution and hydrolysis to occur only on controlled surface of
22 the solid medium, recirculating and cooling the liquid that
23 remained after the necessary amount of the liquid was drawn off
24 for the operation of the fuel cell, and introducing seawater to

1 the remaining liquid to make up for the part of the liquid that
2 was drawn off.

3 In accordance with this invention there is further provided
4 a method of making a catholyte solution comprising hydrogen
5 peroxide, including the steps of fabricating a solid medium
6 comprising sodium peroxide particles as a solid catholyte
7 suspended within a matrix of potassium superoxide and/or sodium
8 hydroxide, wherein the solid medium has a controlled surface,
9 dissolution of the solid catholyte and encapsulating species in a
10 liquid circulating across the controlled surface of the medium,
11 wherein said matrix of potassium superoxide and/or sodium
12 hydroxide controls the rate of the dissolution and hydrolysis of
13 the solid catholyte by allowing for dissolution to occur only on
14 the controlled surface of said medium, recirculating and cooling
15 the liquid that remained after the necessary amount of the liquid
16 was drawn off for the operation of the fuel cell, and introducing
17 seawater to the remaining liquid to make up for the part of the
18 liquid that was drawn off.

19 These and other features of the present invention will
20 become apparent from the following detailed description when
21 taken in conjunction with the accompanying drawings.

BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1 shows graphically the short term stability of hydrogen peroxide; and

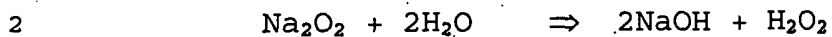
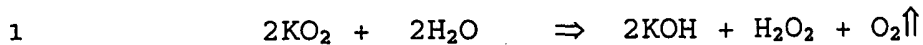
FIG. 2 is a schematic illustration of the system of this invention.

DESCRIPTION OF THE PREFERRED EMBODIMENT

This invention provides a system and a method of storage of a solid catholyte, wherein the solid catholyte is stored in a solid medium, and a subsequent dissolution and hydrolysis of the catholyte for use in electrochemical cells that are used in torpedoes, UUVs, and other undersea vehicles.

The present invention lies in the reactions of oxides, peroxides, and superoxides of alkaline metals with water and their hydrolysis to produce hydroxides, hydrogen peroxide, and oxygen, depending on the chemical compound used for hydrolysis. Hydrogen peroxide is the cathode species used in semi fuel cells in undersea vehicles. This system and method provide for hydrogen peroxide as a cathode species avoiding, however, high safety risks associated with storing and the transportation of liquid hydrogen peroxide.

The hydrolysis reactions of potassium superoxide and sodium peroxide yield the hydrogen peroxide necessary for operation of aluminum-hydrogen peroxide semi fuel cell from a dry storage form. These reactions are as follows:



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4 The powdered or crystalline form of sodium peroxide and
5 potassium superoxide lends itself to rapid dissolution with an
6 exothermic reaction. The heat that is generated during the
7 hydrolysis is detrimental to the stability of hydrogen peroxide
8 formed during the reaction. FIGURE 1 shows results of a hydrogen
9 peroxide concentration test where 4% per hour decomposition rate
10 of unstabilized hydrogen peroxide was observed.

11 Although drop in hydrogen peroxide concentration would not
12 present a problem in short torpedo type missions, it would reduce
13 system energy density in applications of long duration. It is
14 necessary then to control the hydrolysis rate of the dry
15 catholyte to limit its production to the rate at which it is
16 consumed in the semi fuel cell.

17 According to the present invention, the rate of dissolution
18 of a solid catholyte can be limited by providing a solid cake of
19 reactant species where the hydrolysis is allowed to occur on a
20 specific controlled surface instead of over the entire surface of
21 multiple fine particles of the catholyte. As the alkaline metal
22 oxides lack thermal stability, the process of casting a solid
23 cake is not possible for most of the oxides. However, a solid
24 cake can be formed as a solid medium comprising solid catholyte
25 particles suspended within a matrix of encapsulating species when

1 the encapsulated species have melting temperatures below the
2 thermal decomposition temperature of the solid catholyte.

3 Accordingly, a solid medium of this invention includes, in
4 addition to a solid catholyte, an encapsulating species to enable
5 formation of a stable entity and at the same time to control
6 dissolution of the solid catholyte from a controlled surface of
7 the solid medium into a working liquid catholyte by flow of the
8 catholyte over the controlled surface. The encapsulating species
9 limits the access of the hydrolyzing liquid to catholyte
10 particles present on the controlled surface only. The controlled
11 surface is that portion of the solid medium where the hydrolysis
12 actually occurs.

13 Solid catholyte for the solid medium of this invention is
14 selected from alkaline metal oxides, superoxides, and peroxides
15 and the encapsulating species is selected from alkaline metal
16 oxides, superoxides, and peroxides and sodium hydroxide such that
17 the melting temperature of the encapsulating species is below the
18 thermal decomposition temperature of the solid catholyte.
19 Preferably the solid catholyte is sodium peroxide particles and
20 the encapsulating species is a matrix of potassium superoxide
21 and/or sodium hydroxide. The preferred particle size of the
22 sodium peroxide ranges from 0.03" to 0.12". The preferred amount
23 of the sodium peroxide in the solid medium is about 65-75% by
24 weight.

1 FIG. 2 shows a preferred embodiment of this invention. This
2 embodiment provides for a system of storage and subsequent
3 dissolution of a solid catholyte. It includes a solid medium
4 comprising sodium peroxide particles suspended within a matrix of
5 potassium superoxide and/or sodium hydroxide. This solid medium
6 provides completely consumable materials for a semi fuel cell as
7 the encapsulating species (potassium superoxide and/or sodium
8 hydroxide) are also useful in the operation of the fuel cell and
9 are used up in the cell in addition to the products of hydrolysis
10 of the solid catholyte.

11 In FIG. 2, dissolution of solid medium 1 and, at the same
12 time, solid catholyte particles 2 and encapsulating species 4 is
13 accomplished by ablation of solid medium 1 from controlled
14 surface 10. Liquid supply 14 that is a water solution of the
15 products resulting from the hydrolysis of solid catholyte
16 particles 2 and encapsulating species 4 is circulated across the
17 controlled surface 10 of medium 1 to dissolve and hydrolyze solid
18 catholyte and encapsulating species and produce hydrogen peroxide
19 while other products are also produced depending on the specific
20 chemical composition of the solid medium. While some of liquid
21 working catholyte 16 is drawn off for use in semi fuel cell 8,
22 the remaining liquid working catholyte 16 is recirculated and
23 cooled through recirculation loop 12 to reduce the heat build up
24 resulting from the process of hydrolysis. As a portion of liquid
25 working catholyte 16 is drawn off for use by semi fuel cell 8,

1 seawater supply 18 is introduced to recirculating loop 12 to make
2 up additional solution. Various cooling means for recirculating
3 loop 12, such as tube in tube, tube and shell heat exchanger, or
4 heat exchanger integrated to the underwater vehicle hull, and
5 various means for introducing seawater to recirculating loop 12,
6 such as pumps and valves, can be used with the present invention.

7 This system and method have several advantages. The solid
8 medium provides for high system energy density, increases shelf
9 life, and provides for low cost in long term storage of the
10 concentrated solid catholyte without the safety risks that are
11 associated with the storage of liquid hydrogen peroxide. As both
12 the solid catholyte and the encapsulating species are used for
13 the operation of the aluminum-hydrogen peroxide semi fuel cell, a
14 savings of over 40% in electrolyte/catholyte species weight that
15 needs to be stored onboard an undersea vehicle is possible when
16 using the system of this invention, as compared to 50% hydrogen
17 peroxide and 50% sodium hydroxide solutions. This system and
18 method allows for a smaller size of an energy system or longer
19 mission duration within the same weight allocation. The
20 materials used as a solid catholyte and encapsulating species are
21 staple items of commerce and do not require further expensive
22 development costs.

23 The additional advantage of this system and method is that
24 transportation restrictions associated with liquid hydrogen
25 peroxide are avoided. The air shipment of alkaline metal oxides

1 is permitted within certain parameters while concentrated
2 hydrogen peroxide cannot be shipped. This allows for the use of
3 this system and method at remote sites where air transportation
4 is the only reasonable method of delivering material.

5 In addition to the Navy applications of this invention in
6 torpedoes, UUVs, etc., there exist numerous possible commercial
7 applications of this invention, for example, in the area of
8 undersea exploration such as deep sea search, rescue, and
9 discovery and oil platform surveillance as well as applications
10 in physical oceanography, for example, in remote water sampling.

11 While the present invention has been described with respect
12 to the preferred embodiments thereof, it will be understood by
13 those of ordinary skill in the art that many variations and
14 modifications can be effected within the scope and spirit of this
15 invention.